HAZARD EVALUATION AND TECHNICAL ASSISTANCE REPORT
HETA 89-379 & 90-282-L2074
STONE CONTAINER CORPORATION
MISSOULA, MONTANA
OCTOBER 1990

Hazard Evaluations and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations and Field Studies
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I. INTRODUCTION

On September 27, 1989, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Stone Container Corporation to investigate a problem in the color removal plant of Stone Container's Missoula plant. The requestor described a problem of headaches and light headedness when workers were in the color removal plant. On December 12-14, 1989, NIOSH investigators conducted an initial environmental survey at the color removal plant. During this survey, background information on the nature of the request was obtained, reports of previous environmental investigations were reviewed, a walk-through survey of the building was conducted, and environmental samples were collected in the building. A return visit to the plant was scheduled to conduct quantitative sampling for one of the contaminants qualitatively identified during the December survey. The color removal plant was shut down from February until mid June, 1990, so a return visit was conducted on July 19-22, 1990. In this intervening time, on May 22, 1990, an additional request to conduct a health hazard evaluation was received from Stone Container Corporation employees who worked in the Old Corrugated Cardboard (OCC) plant. The requestors were concerned about exposures to dusts in the OCC where the workers had been complaining about irritation to the eyes, nose, throat, and lungs. An environmental survey was planned at the OCC to coincide with the return visit to the color removal plant on July 19-22.

II. BACKGROUND

The Stone Container Corporation Missoula Plant produces paper products for use in cardboard containers. The color removal plant (CRP) is an auxiliary step in the plant's waste water treatment. The purpose of the unit is to clarify up to 10 million gallons per day (mgd) of wastewater by removing color from the plant's waste stream before it is discharged into an adjacent river. The color removal facility is a singal building about 20,000 square feet in size and located at the southern end of the Stone Container property. the building houses three open surface tanks, a closed sludge tank, a small control room, and several storage tanks. The wastewater enters the first mix tank where a coagulant polymer is added and thoroughly mixed with the wastewater. Once mixed, the polymer begins to coagulate the color in the wastewater to form a small floc. A flocculent is then added to the mix as it flows into the second tank where a larger floc is formed. The large floc is mechanically separated in the 100-ft diameter dissolved air flotation (DAF) clarifier using air bubbles to float the floc to the surface where it is skimmed into a sludge tank. The thick sludge has a high BTU content and is burned in the recovery boilers as a supplemental fuel.

The CRP has a large ventilation system which has the capacity to exchange the air every 2.5 minutes. The air exchange rate is rarely this high except in the summer months. There are two large roof vents which allow for exhausting building air and two large bay doors which are often kept open when the weather permits. However, in cold weather, the roof vents and doors are kept closed and the outside air louvers are closed down to prevent freezing of the water in the plant.

The CRP requires very little manpower to operate as it is fully automated. Operators spend only a few hours each week in the area. Health problems in the color removal plant occur primarily when maintenance workers are in the plant, usually welding metals that are inside one of the three open tanks. The maintenance workers all described the problem as an intense headache that developed suddenly along with nausea and lightheadedness.

The old corrugated cardboard (OCC) plant receives used cardboard material in rail and truck cars, and the material is fed via a conveyor belt into a pulper where the recycled material is processed into new cardboard pulp. The area of concern was in the warehouse where an operator unloads cardboard bales from rail cars and trucks, stacks the material, and then loads it onto the conveyor belt which leads to the processing area. Part of the job entails cleaning the rail cars and trucks and keeping the warehouse floor and the forklift trucks clean. The main job is to keep the conveyor line full of cardboard bales. Operators complained of eye, nose, and throat irritation due to the high dust levels encountered while loading and unloading bales and especially while cleaning the cars and floors.

III. MATERIALS AND METHODS

The December CRP survey consisted of: (1) an inspection of the color removal plant and the process operation; (2) interviews with operators of the CRP, maintenance workers who had worked in the CRP, and management representatives; and (3) an environmental survey designed to identify and quantitate the airborne contaminants in the CRP.

During the December survey, all outside air vents were closed in the CRP to simulate very cold weather conditions. The qualitative analysis work from this visit identified methyl disulfide as a potential contaminant. For the subsequent visit in June, welding activities were simulated without shutting down the plant. Two pieces each of mild steel and stainless steel were soaked in the second mix tank and the in digestor tank for several weeks prior to the visit. During the June survey, the steel pieces were retrieved and welded for 15 minutes each while breathing-zone air samples were collected for methyl disulfide and metal fumes. This was done for each of the four steel pieces. The worker conducting this experiment wore a self-contained breathing apparatus during the tests.

The specific measurements and types of samples collected in the environmental surveys are detailed in the following list.

A) Personal breathing-zone samples for hydrogen sulfide were collected using Draeger 5/a-L long-duration detector tubes. The samples were collected using an SKC model 222 low-flow sampling pump at 20 cubic centimeters per minute (cc/min). The airborne concentrations were calculated immediately following collection.

B) Instantaneous measurements of hydrogen sulfide and percent oxygen were made throughout the CRP at different times during the day. These measurements were made using a Scientific Industrial model HMX271 monitor. The model HMX271 had sensors for combustible gases, percent oxygen, and hydrogen sulfide (H_2S). The instrument belonged to Stone Container Corporation and was calibrated for H_2S just prior to use.

C) Air samples were collected for inorganic acids (i.e., hydrochloric, hydrofluoric, nitric, phosphoric, sulfuric, and hydrobromic acids) on 600-milligram (mg) silica gel tubes at flow rates of 50 cc/min using SKC model 222 low-flow sampling pumps. The samples were analyzed according to NIOSH Method 7903 using ion chromatography[1].

D) Air samples for qualitative analysis of unknown contaminants were collected on 150-mg charcoal and silica gel tubes at flow rates of 50 to 200 cc/min using the SKC model 222 low flow pumps. The samples were extracted with carbon disulfide and analyzed by gas chromatography-mass spectrometry.

E) Air samples for metal fumes were collected during the June survey in the CRP on cellulose ester filters at flow rates of 2.0 liters per minute (Lpm) using Gillian model HFS 513A high flow pumps. Analysis was done according to NIOSH method 7300 using an inductively coupled plasma emission spectrometer (ICAP)[1].

F) Air samples collected for methyl disulfide were collected on 150-mg charcoal tubes at flow rates of 0.2-1.0 Lpm. Analysis was accomplished using an experimental method which entailed desorption of the analyte from the tube with 1.0 mL of methylene chloride, separation with a 30-m fused silica capillary column containing SPB-1, and analysis by gas chromatography using a flame photometric detector.

G) Personal breathing-zone total dust samples were collected in the OCC on mixed cellulose ester membrane filters at a flow rate of 2.0 Lpm. The filters were analyzed gravimetrically according to NIOSH method 0500[1].

IV. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week, for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus, such contact may increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent becomes available.

The primary sources of air contamination criteria generally consulted include: (1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs); (2) the American Conference of Governmental Industrial Hygienist's (ACGIH) Threshold Limit Values (TLVs)[2]; and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) standards[3]. These sources provide environmental limits based on airborne concentrations of substances to which workers may be occupationally exposed in the workplace environment for 8 to 10 hours per day, 40 hours per week for a working lifetime without adverse health effects.

A discussion of the substances evaluated in this survey is presented below. The industrial evaluation criteria for the substances evaluated in this survey are also included. A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits (STELs) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

A. Hydrogen Sulfide

Hydrogen sulfide (H_2S) is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations. Prolonged exposure to 250 parts per million (ppm) may cause pulmonary edema. Prolonged exposure to levels as low as 50 ppm may cause rhinitis, pharyngitis, bronchitis, and pneumonitis. Repeated exposure to H_2S results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without any effect. Rapid olfactory fatigue can occur at high concentrations. Acute exposures may result in headaches, dizziness, irritation of the eyes and nose, and upset stomach[4].

The current OSHA PEL and ACGIH TLV for hydrogen sulfide are both 10 ppm as 8-hour time-weighted averages (TWAs) and 15 ppm as a 15 or 30-minute short-term excursion limit. NIOSH currently recommends 10 ppm as a 10-minute ceiling value (not to be exceeded during any 10-minute period during the day).

B. Methyl Disulfide (dimethyl disulfide)

Not much information is available on the health effects to humans of methyl disulfide (MDS). Animal data suggest that MDS may be broken down to methyl mercaptan in the body. Breathing vapors of MDS may cause headache, dizziness, nausea and vomiting. Massive exposures may cause loss of consciousness and death. MDS is also an eye and skin irritant. There are no evaluation criteria established for MDS. For a point of comparison, the OSHA PEL and ACGIH TLV for dimethyl sulfate is 0.1 ppm as an 8-hour TWA.

C. Total Dust

Particulate aerosols which do not show a marked toxic effect and are not otherwise classified are lumped into a category of nuisance dusts. These dusts have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. Excessive exposures to nuisance dusts in the workplace may reduce visibility, may cause unpleasant deposits in the eyes, ears, and nasal passages, or cause injury to the skin or mucous membranes. The current OSHA PEL for Particulates Not Otherwise Classified (PNOC) is 15 milligrams per cubic meter of air (mg/m3) measured as total dust. The ACGIH has a TLV of 10 mg/m3 for PNOC measured as total dust[4].

V. RESULTS

A. Color Removal Plant (CRP)

The hydrogen sulfide levels measured during the December survey are summarized in Table 1. The obvious source of H_2S was from the second mix tank where levels as high as 27 ppm were found directly above the liquid in the tank. The levels in the rest of the building were quite uniform; a result of the large volume of air being circulated in the building. The outside air intakes had been shut-down for the sampling which resulted in the H_2S levels continuing to build throughout the day. The levels measured on 12-14-89 when the exhaust vent was open to the outside is probably a more accurate estimate of typical levels. These measurements do emphasize the need to insure that at least one of the roof exhaust vents is open at all times.

Hydrogen sulfide levels were again checked during the June visit when the CRP was operating under normal conditions. That is, both the front and rear bay doors were open a few feet, one of the roof exhaust vents was open (above the second mix tank) and all the outside air louvers were closed. The Company's Industrial Scientific H_2S monitor was used to take the readings. Ambient levels on the floor area where the welding experiment took place were about 3 ppm H_2S. Levels above the first mix tank were about 15 ppm directly above the liquid. Concentrations went as high as 40-60 ppm directly above the liquid in the second mix tank where there was liquid agitation. Concentrations on the catwalk adjacent to the second mix tank were 4-5 ppm. Once again, the second mix tank was a source for high H_2S concentrations, however, the room ventilation prevented the H_2S from accumulating and reaching high concentrations.

All the other samples collected during the December survey resulted in levels which were below the analytical limit of detection, except for one sample analyzed by gas chromatography-mass spectrometry (GC-MS). A copy of the reconstructed ion chromatogram from the GC-MS analysis is enclosed with identified peaks labeled (see Figure 1). While the concentrations were low, several compounds were identified including dimethyl disulfide (methyl disulfide), chloroform, dichloro-propanols, dimethyltri- and tetrasulfides, terpenes and terpene derivatives, and toluene. Three remaining charcoal tube samples were analyzed directly for methyl disulfide (MDS) following the GC-MS findings. Only one of these samples were found to contain MDS, and that only at a trace level (1.2 microgram per liter, ug/L).

All four samples collected for inorganic acids resulted in non-detectable results (limit of detection was 3-5 ug per sample).

Ten charcoal tube samples were collected during the simulated welding operation in the CRP in June. Only one sample had a detectable amount of MDS, resulting in a trace air concentration of 0.3 ug/L.

Four metal fume samples collected during the welding experiment resulted in several metals being found but generally at low concentrations. One of the samples collected during the welding of the mild steel sample that had soaked in the clarifier resulted in a 15-minute concentration of 5.5 milligrams per cubic meter (mg/M^3) for calcium oxide (OSHA PEL for 8-hr TWA is 5 mg/M^3), 13.4 mg/M^3 for iron oxide fume (OSHA 8-hr PEL is 10 mg/M^3), and 2.7 mg/M^3 for manganese (OSHA ceiling value is 3 mg/M^3 and 8-hr TWA is 1 mg/M^3). While none of these results were above the respective limits since they were short-term exposures, they are high enough to be a concern if someone was welding for long periods in a confined tank.

B. Old Corrugated Cardboard (OCC) Plant

The results of the total dust samples collected in the OCC are summarized in Table 2. The two operators averaged 2.6 and 1.2 mg/M^3 of total dust exposure. Both these values are below the ACGIH TLV of 10 mg/M^3 and the OSHA PEL of 15 mg/M^3. The dust consisted of cellulose fibers and "road dust" from the inside of the rail/truck cars and from the cardboard bales themselves. The highest dust levels were encountered when the operator cleaned his forklift truck using compressed air. This concentration, 40 mg/M^3, was quite high but only lasted about 10 minutes. There is no short-term exposure limit for nuisance dust.

VI. DISCUSSION AND CONCLUSIONS

The major exposures in the color removal plant (CRP) are to hydrogen sulfide. Depending on the weather and the amount of outside air being circulated in the CRP, ambient levels of 2-5 ppm throughout the plant would be common. Much higher levels can be found closer to the second mix tank, which is the major source of H_2S in the building. Trace levels of methyl disulfide (dimethyl disulfide) and other sulfides were also identified from GC-MS samples collected in the CRP. The symptoms described by the maintenance workers were quite consistent in that they all reported immediate and intense headaches followed by nausea and dizziness. While these symptoms have all been associated with acute exposure to H_2S, generally other symptoms, such as eye irritation, usually accompany H_2S exposure and are often the first symptoms to be reported with low level H_2S exposures. For these reasons, it was thought that the exposures might be from another contaminant which caused the immediate and intense headaches. The toxicology data on methyl disulfide and other sulfides (or sulfur compounds) is less well documented than H_2S, but suggests health effects similar to H_2S. Whether the symptoms reported are from H_2S or another compound, they are clearly coming from the same source, the second mix tank. It is also likely that the sludge in the bottom of the other two tanks would emit significant amounts of H_2S and other sulfur containing compounds. Precautions, such as those outlined in the Recommendations section, should be taken when working in the CRP and particularly when working inside a drained tank.

The dust exposures in the OCC warehouse were below any occupational health evaluation criteria. The characteristics of the dust suggest that it may be irritating and a potential allergen. Therefore, there may be some workers who have trouble working around the dust. The practice of dry sweeping and cleaning with compressed air were obvious sources of high dust exposures that should be discontinued. The use of bales of cardboard being pushed by forklift trucks to sweep the floors was also a practice which was effective but resulted in the dust becoming airborne.

VII. RECOMMENDATIONS

1. Outside air in the CRP should be kept to a maximum, whenever the weather permits, to prevent accumulation of H_2S. When workers have to enter the CRP and the outside air louvers are closed due to cold weather, the bay doors should be opened prior to workers entering the building. The H_2S levels should be checked upon entry when the chance for vapor accummulation exists.

2. When the tanks are drained and workers are entering them for repair work, a confined entry procedure should be taken. That is, the H_2S and percent oxygen levels should be measured by a safety representative, a buddy system with an attached safety line should be used, and air-supplied respirators should be worn to prevent the problems that have appeared in the past. At the time of the June visit, a supplied air respirator cart had been nearly assembled which included a tank of breathing air, hoses and a full-face respirator for air-supplied operation. This cart should be utilized in the CRP for repair activity. Use of respirators in this area should be incorporated into the plant respirator program.

3. Since the second mix tank is the major source of H_2S in the CRP, a stationary monitor for H_2S should be considered on the catwalk adjacent to this tank. There currently is a stationary monitoring point between the sludge tank and the polymer storage tank. This H_2S monitoring system should be able to accommodate another monitoring point.

4. An alternative method for cleanup in the OCC warehouse should be considered. The use of compressed air for blowing down equipment should particularly be discontinued.

VIII. REFERENCES

1. NIOSH (1984). Manual of analytical methods: 3rd edition, Vol. 1. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health (NIOSH), DHHS (NIOSH) Publication No. 84-100.

2. Threshold Limit Values and Biological Exposure Indices for 1989-1990. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

3. 29 CFR 1910.1000 (March 1989). Code of federal regulations. Washington, DC: U.S. Government Printing Office of the Federal Register.

4. Occupational Health Guidelines for Chemical Hazards. National Institute for Occupational Safety and Health and Occupational Safety and Health Administration. January 1981. DHHS (NIOSH) Publication No. 81-123.

TABLE 1
SUMMARY OF HYDROGEN SULFIDE MEASUREMENTS
IN THE COLOR REMOVAL PLANT
STONE CONTAINER CORPORATION
MISSOULA, MONTANA
DECEMBER 12 AND 14, 1989

Location	Time	Sample Type*	Concentration (ppm)
December 12, 1989			
On top of rotor in center of clarifier tank	10:25 to 14:30	LDDT	4.2
First mix tank, on rim	14:35 to 16:50	LDDT	7.6
First mix tank, near inlet	10:30	STDT	4 - 6
Sludge tank at vent hole	10:45	STDT	4 - 6
Control room	14:30	STDT	6 - 8
Operating area	14:35	STDT	6 - 8
Control room	18:20	meter	11 - 12
Adjacent to H_2S alarm	18:20	meter	12 - 13
Sludge tank vent hole	18:22	meter	8
Top of sludge skimmer tank	18:24	meter	12 - 13
Above (4-in) liquid in 1st tank	18:26	meter	18 - 23
Second mix tank, at surface	18:27	meter	27
Flocculant adding station	18:28	meter	13 - 14
Center of skimmer tank	18:30	meter	13 - 14
Above liquid in skimmer tank	18:30	meter	13 - 14
SE corner of building	18:35	meter	12 - 13
SW corner of building	18:36	meter	13
Top of skimmer tank & above liq	18:46	meter	13
General level in building	18:50	meter	13
December 14, 1989			
First mix tank, on rim	8:39 to 12:36	LDDT	5.3
General level in building	8:45	meter	3 - 5

*LDDT - long duration detector tube
STDT - short-term detector tube
meter - Industrial Scientific Model HMX271 hydrogen sulfide monitor

TABLE 2
SUMMARY OF TOTAL DUST MEASUREMENTS
IN THE OLD CORRUGATED CARDBOARD PLANT
STONE CONTAINER CORPORATION
MISSOULA, MONTANA
JUNE 21, 1990

Operator/Area	Time On	Time Off	Conc. (mg/M^3)	Comments
Assistant Oper.	07:10	08:54	1.8	Loading, stacking, cleaning
	08:54	11:06	1.6	Unloading rail cars, cleaning
	11:06	11:16	40.0	Cleaning forklift with compressed air
	11:16	13:23	2.2	Plant went down at 12:30, working in plant repair
	13:23	14:47	1.5	
TWA			2.6	
Asst. Oper Train	07:12	09:05	2.7	Trainee, same job as oper.
	09:05	11:07	0.9	
	11:07	13:21	0.6	Plant down at 12:30
	13:21	14:47	0.5	Continue stacking/cleaning
TWA			1.2	
Area on desk	07:16	11:04	1.0	On desk where workers break
	11:04	14:48	0.4	
Average			0.7	